STUDIES ON REACTION BETWEEN GAS AND SOLID. VI. AZOTATION OF CALCIUM CARBIDE AND THE EFFECT OF CATALYSERS ON ITS VELOCITY.[1]

By Takeo AONO.

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It has been known that the most effective and technically important catalysers for the reaction of calcium carbide with nitrogen to form calcium cyanamide are chloride and fluoride of calcium.[2] In the present work the effects of catalysers of various kinds in various quantities upon some kinds of technical carbide have been experimentally studied.

Experimental.

1. Calcium Fluoride. The samples of carbide (powdered) and the method employed were similar to those of the former experiments for the determination of the effect of temperature upon the same reaction. The results are shown in Table 1 and Figs. 1 and 2. The temperature was kept at 1000°C. The samples of carbide of Exp. No. 362, 375, 391, 392, 393, 394 were the same, while that of No. 425 was taken from another source. Fig. 2 was obtained from Fig. 1 by integrating the velocity graphically and comparing the final values with the results of analyses of the products.

Similar results were obtained with "granular carbide," which was prepared by K. Hibi's method in a spherical grain of about 1–2 mm. in diameter. The temperature was kept at 1140°C. (Tables 2, 3 and Fig. 3). Taking the quantity of calcium fluoride added to the carbide as abscissa, and the time (in min.) required to reach definite degrees of azotation as ordinate, we have Fig. 4.

From these experimental results we see that there is an optimum quantity of fluoride to be added to the carbide, as was reported by F. Foerster and H. Jacoby.[3] The optimum quantity is a function of reaction temperature and kinds of carbides; for instance, no effect being perceived by adding CaF_2 at 870°C.

It is also interesting that the point of the maximum velocity is also a function of the quantities of CaF_2 added, the larger the quantity, the later comes the point (Table 4).

(1) Read before the meeting of the Chemical Society of Japan in Dec. 1931.
(2) F. Foerster and H. Jacoby, *Z. Elektrochem.* **12** (1907), 101. G. Bredig, W. Fraenkel and E. Wilke, ibid. **13** (1907), 605. Polzeniuss, D. R. P. Nr. 163320, Kl. 12k (1901).
(3) F. Foerster and H. Jacoby, *Z. Elektrochem.* **12** (1907), 101.

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Table 1.

Azotation velocity of powdered carbide with various quantities of calcium fluoride at const. temp. of 1000°C.

Exp. No.	375		391		392		393		394		425	
$+CaF_2$	6 *u**		11 *u*		4 *u*		2.5 *u*		1 *u*		0 *u*	
CaC_2 %	66.8		64.2		68.5		69.5		70.6		74.4	
Sample, gr.	3.0012		3.3011		3.0929		3.0011		3.0012		3.0135	
Time, min.	vel.	fix. %	vel.	fix. %	vel.	fix. %	vel.	fix. %	vel.	fix. %	vel.	fix. %
1		0.02	0.07	0.14	0.07	0.14	0.09	0.16	0.09	0.19	0.175	0.29
2		0.07	0.08	0.29	0.08	0.30	0.13	0.39	0.14	0.40	0.24	
3	0.068	0.18	0.09	0.46	0.11	0.49	0.20	0.72	0.24	0.76	0.30	0.87
4	0.10	0.35	0.11		0.14	0.75	0.29	1.21	0.40	1.41	0.33	1.51
5	0.15	0.57	0.14	0.94	0.18		0.40	1.89	0.73	2.62	0.33	2.19
6	0.18	0.83	0.17		0.22	1.51	0.53	2.81	1.21	4.54	0.325	
7	0.21	1.23	0.20	1.65	0.26	2.03	0.72	4.06		7.55	0.315	3.53
8	0.31	1.72	0.23		0.33	2.64	1.05	5.91	1.92	11.50	0.303	
9	0.38	2.36	0.26	2.62	0.43	3.44	1.60	8.83	1.61	15.29	0.294	
10	0.47	3.11	0.30	3.22	0.57	4.50	2.85	13.44	1.28	18.34	0.283	5.39
12	0.80	5.33	0.43	4.78	1.04	7.87	3.76	27.85	1.07	23.36	0.26	
14	1.25	9.01	0.63	7.01	2.22	14.54	2.50	41.08	0.93	27.63	0.24	
16	2.015	15.22	0.90	10·23	2.50	24.62	1.46	48.95	0.81	31.36	0.22	
18	2.02	22.75	1.19	14.56	1.67	33.83	0.88	53.70	0.69	34.55	0.203	
20	1.84	29.96	1.43	20.10	1.15	39.54	0.71	56.90	0.58	37.21	0.185	10.14
25	1.08		1.14	34.90	0.80		0.52	62.90	0.51	43.10	0.160	
30	0.82	50.97	0.96	45.86	0.56	56.59	0.38	67.45	0.44	48.25	0.155	13.54
35	0.63		0.73	54.82	0.41		0.35	71.00	0.39		0.146	15.08
40	0.53	62.95	0.55	61.55	0.35	65.90	0.30	74.50	0.37	56.60	0.135	16.56
45	0.43		0.45		0.31	69.40	0.22	77.10	0.35	60.40	0.128	17.92
50	0.32	70.72	0.37	71.10	0.23	72.20	0.17	79.10	0.31	63.90	0.12	19.21
60	0.21	75.60	0.19	77.00	0.17	76.35	0.11	81.85	0.245	69.85	0.104	21.53
70	0.13	78.35	0.10		0.11	79.35	0.07	83.60	0.19	74.45	0.10	23.60
80	0.09	80.00	0.06	80.95	0.08	81.35	0.045	84.75	0.145	78.05	0.095	25.56
90	0.06	81.30	0.03	82.45	0.06	82.75	0.025	85.55	0.095	80.40	0.088	27.50
100	0.05	82.20	0.025	83.10	0.04	83.90	0.020	85.95	0.07	82.15	0.080	29.20
120	0.02	83.15	0.013	83.80	0.024	85.10	0.008	86.50	0.036	84.25	0.077	32.45
140			0.007	84.20	0.014	85.80	0.003	86.65	0.018	85.45	0.074	35.56
160					0.007	86.10			0.011	85.85	0.068	38.48
180					0.004	86.15			0.006	86.20	0.065	41.25
200					0.003	86.20						

* To the author's regret, the unit "*u*" cannot be explained here.

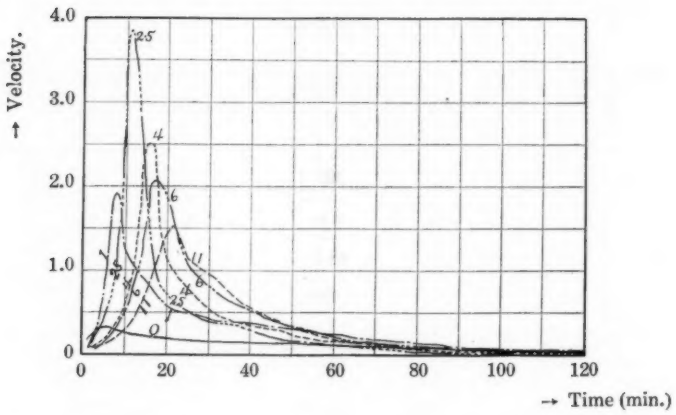

Fig. 1. Azotation velocity of powdered carbide at 1000°C., the numbers on the curves indicating the quantity of CaF_2 added. (in unit "u").

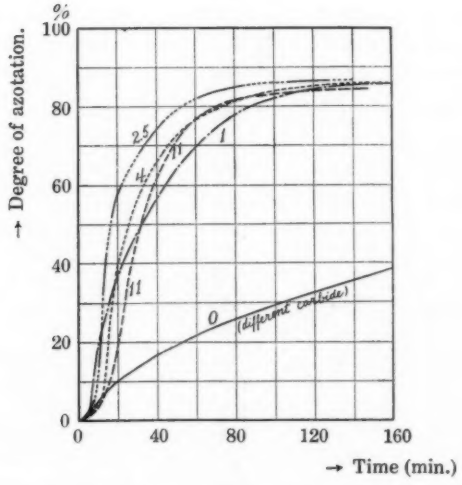

Fig. 2. Effect of CaF_2 upon the azotation of powdered carbide at 1000°C. The numbers on the curves indicate the quantity of CaF_2 added (in unit "u").

Table 2.

Azotation velocity of "granular carbide" with calcium fluoride at constant temp. of 1140°C. Using reaction tube A.

Exp. No.	376		378		379	
$+CaF_2$	0		0		3 u	
Carbide %	62.9		72.1		69.2	
Sample gr.	3.0036		3.0043		3.0004	
Time, min.	vel.	fix. %	vel.	fix. %	vel.	fix. %
1	1.11	1.70	0.68?	1.06		(0.54)
2	1.30	4.08	0.833	3.39	0.588	1.99
3	1.35	6.61	0.82	5.90	0.908	4.33
4	1.36	9.19	0.78	8.33	1.176	7.75
5	1.35	11.75	0.73	10.59	1.25	11.72
6	1.33	14.28	0.68	12.73	1.00	15.32
7	1.32	16.78	0.66	14.71		18.32
8	1.29	19.25	0.63	16.66	0.80	21.00
9	1.27	21.68	0.61	18.55	0.715	
10	1.24	24.05	0.60	20.40	0.715	25.70
12	1.18	28.63	0.58	23.94	0.55	29.73
14	1.12	33.02	0.55	27.36	0.53	33.34
16	1.06	37.40	0.51	30.65	0.48	36.58
18	0.995	41.10	0.50	33.78	0.46	39.68
20	0.939	44.75	0.49	36.78	0.44	42.58
25			0.44		0.40	49.65
30	0.701	60.02	0.415	50.40	0.37	55.75
35			0.38		0.33	61.40
40	0.464	71.10	0.35	61.95	0.28	66.35
45					0.24	
50	0.192	77.0	0.26	71.10	0.19	75.60
60	0.064	79.2	0.175	77.55	0.09	80.00
70	.0.025	79.9	0.080	81.25	0.02	81.55
80	0.000	80.0	0.025	82.70	0.00	81.70
90			0.000	82.90		

Table 3.

Azotation velocity of "granular carbide" with calcium fluoride at constant temp. of 1140°C. Using reaction tube B.

Exp. No.	390		382		383		384		385	
$+CaF_2$	0		6 *u*		10 *u*		2 *u*		4 *u*	
Carbide %	72.3		68.1		65.2		70.3		69.3	
Sample, gr.	3.0008		3.0029		3.0029		3.0030		3.0010	
Time, min.	vel.	fix. %	vel.	fix. %	vel.	fix. %	vel.	fix. %	vel.	fix. %
1	1.07	1.05		(0.09)	0.167	0.22	0.213	0.33	0.541	0.68
2	1.25	3.48	0.133	0.38	0.220	0.68	1.00	1.55	0.788	2.13
3	1.25	6.10	0.290	1.04	0.267		1.92	5.20	1.30	4.51
4	1.19	8.65	0.371	2.04	0.303	1.94	1.50	9.11	1.37	7.75
5	1.07	10.98	0.425	3.29	0.353		1.40	12.48	1.37	10.92
6	1.04	13.17	0.500	4.73	0.395	3.60	1.25	15.50	1.25	
7	1.00		0.565	6.36	0.423		1.15	18.10	1.15	16.58
8	1.00	17.36	0.588	8.12	0.447	5.64	0.97	20.35	1.07	
9	0.909		0.605	9.94	0.470		0.88	22.35	0.92	21.25
10	0.909	21.29	0.590	11.75	0.490	7.88	0.84	24.25	0.84	23.25
12	0.862		0.545	14.88	0.510	10.28	0.76	27.82	0.788	26.90
14	0.838		0.513	18.42	0.522	12.77	0.74	31.12	0.730	
16	0.769		0.485	21.45	0.525	15.30	0.70	34.25	0.705	33.62
18	0.685		0.460	24.32	0.520	17.84	0.67	37.20	0.667	
20	0.699	37.92	0.445	27.06	0.510	20.29	0.62	40.00	0.640	39.70
25	0.614	44.73	0.405		0.485		0.55		0.59	
30	0.570	50.90	0.390	39.68	0.460	31.82	0.51	52.30	0.55	53.07
35			0.375		0.440		0.46		0.49	
40	0.440	61.50	0.350	51.10	0,415	42.48	0.415	62.80	0.42	64.10
45	0.377			56.25	0.393		0.365		0.375	
50	0.350	69.65	0.300	61.00	0.370	51.90	0.310	70.90	0.31	72.35
60	0.220	75.30	0.210	69.35	0.320	60.20	0.204	76.60	0.17	77.70
70	0.110	78.90	0.150	74.90	0.270	67.30	0.105	79.90	0.08	80.40
80	0.047	80.40	0.080	78.30	0.200	73.00	0.095	81.45	0.025	
90	0.023	81.10	0.040	80.00	0.135	77.10	0.020	82.10	0.000	81.70
100	0.000	81.35	0.021	80.55	0.075	79.50	0.000	83.13		
120			0.000	80.75	0.010	81.15				

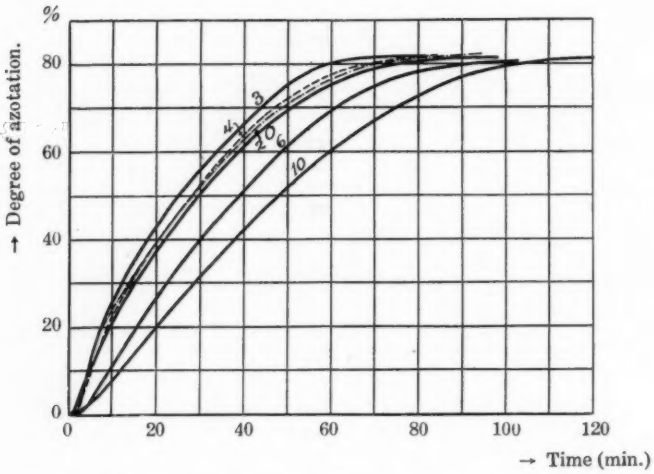

Fig. 3. Effect of CaF_2 upon the azotation of "granular carbide" of 71.0% purity at 1140°C. The numbers on the curves indicate the quantity of CaF_2 added. (in unit "u").

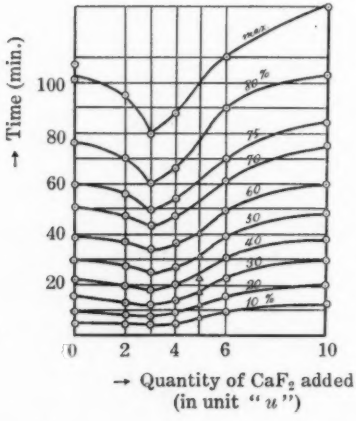

Fig. 4. Time (min.) required to attain to the equal degrees of azotation and the effect of CaF_2 added to the granular carbide of $1 \sim 2$ mm. dia. ($CaC_2 = 71.0\%$)

Table 4.

Effect of CaF_2 upon the time of the velocity maximum.

a) Powdered carbide at 1000°C.

Exp. No.	425	394	393	392	375	391
$+CaF_2$	0 *u*	1 *u*	2.5 *u*	4 *u*	6 *u*	11 *u*
Time of vel. max. (min.)	4.5	8.0	11.3	15.–16.5	17–18.5	21.5

b) "Granular carbide" at 1140°C.

Exp. No.	378	384	379	385	382	383
$+CaF_2$	0 *u*	2 *u*	3 *u*	4 *u*	6 *u*	10 *u*
Time of max. vel. (min.)	2.0–2.5	2.5	4.5–5.0	3.2	9.0	15.0–19.0

2. The Slag of a Phosphorus Furnace. This material was prepared from the slag produced by the reaction of phosphate rock and carbon to prepare phosphorus in an electric furnace. The analysis of the slag is as follows (the components are calculated provisionally as oxides):

P_2O_5	SiO_2	Fe_2O_3	Al_2O_3	Total CaO
1.29	18.36	1.75	16.55	49.40%

The effect upon the azotation velocity of calcium carbide is seen in Table 5.

It is very interesting that the slag has not only the accelerating effect, but it also diminishes the time to maximum velocity; the velocity decreases soon after less than two minutes from the beginning, and it is rather uncertain whether the maximum point really exists or not.

Table 5.

Effect of a phosphorus slag added
3% to the powdered carbide ($CaC_2 = 74.4\%$) at 1000°C.

Exp. No.	421		425	
Slag %	3		0	
Sample, gr.	3.0037		3.0135	
Time	vel.	fix. %	vel.	fix. %
1		(2.57)	0.175	0.29
2	1.21	5.15	0.24	
3	1.08		0.30	0.87
4	0.855	10.45	0.33	1.51
5	(0.730)		0.33	2.19
6	0.625	13.63	0.325	
7	0.590		0.315	3.53
8	0.555	16.18	0.303	
9	0.529		0.294	
10	0.500	18.38	0.283	5.39
20	0.332	26.80	0.185	10.14
30	0.262	33.10	0.155	13.54
40	0.228	38.35	0.135	16.56
60	0.173	46.90	0.104	21.53
80	0.150	53.85	0.095	25.56
100	0.133	59.90	0.080	29.20
120	0.118	65.25	0.077	32.45

3. Calcium Chloride. The action of calcium chloride is eminent even at lower temperatures. There is a point of maximum velocity also in this case; the details will be given later with others.

4. Effect of Carbon and Carbon-containing Substances. In the previous paper[1] the author expressed his opinion that the nascent carbon liberated by the reaction, $CaC_2 + N_2 = CaCN_2 + C$, will be acting as an eminent catalyser for this reaction. To ascertain this problem, the following experiments were carried out, using the same apparatus and the same method hitherto employed. To the carbide powder of 900-mesh fineness and 71.3%

(1) T. Aono, This bulletin, **7** (1932), 247.

purity, a definite quantity of each "Darco carbon" (an active carbon), technical calcium cyanamide (21.68% N and 13.3% C) and calcium chloride (previously ignited and dehydrated) was added respectively and subjected to nitrogen at the same temperature (870°C.) and pressure (1 atm.) and the velocity of azotation was compared with the carbide without any added substance. The results are shown in Table 6, Figs. 5 and 6.

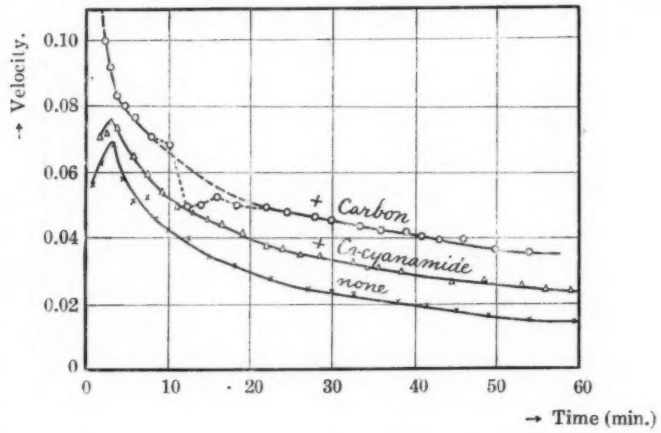

Fig. 5. Azotation velocity of powdered carbide at 870°C. with various catalysers.

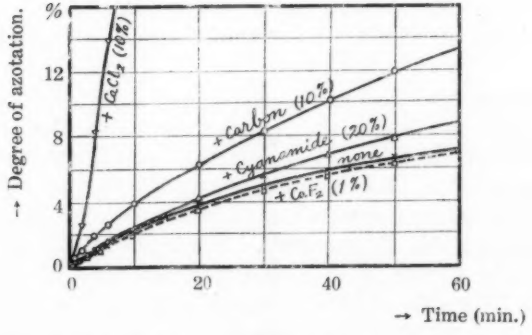

Fig. 6. Effect of various catalysers upon the azotation of powdered carbide at 870°C.

Table 6.

Effect of catalysers on the azotation of carbide power at 870°C. and 1 atm. pressure.

Exp. No.	524		525		521		523		361**	
Catalyser added %	0		Cyanamide, 20		"Darco C," 10		$CaCl_2$, 10		CaF_2. 1	
Sample. gr.	2.7023		2.702+0.543		2.741+0.274		2.736+0.274		4.043	
Time, min.	vel.	fix. %	vel.	fix. %	vel.	fix. %	vel.	fix. %	vel.	fix. %
1	0.0567	0.22					0.345	1.09		0.17
2	0.0633	0.46	0.0715	0.50	0.1070	1.10	0.625	2.62	0.0512	0.40
3	0.0690		0.0752	0.78	0 0925		0.835	5.05	0.0530	0.65
4	0.0655	1.02	0.0727	1.06	0.0830	1.91	1.000	8.35	0.0528	0.90
6	0.0520	1.49	0.0640	1.57	0.0770	2.61	0.715	13.90	0.0462	1.37
	0.0470		0.0578	2.03	0.0714		0.600	18.33	0.0396	1.77
10	0.0424	2.28	0.0525	2.45	0.0680	3.89	0.545	22.20	0.0358	2.13
15	0.0345	3.12	0.0456				0.455	30.65	0.0270	2.89
20	0.0298	3.79	0.0400	4.18	0 0500	6.21	0.393	37.78	0.0250	3.53
30	0.0243	4.96	0.0333	5.59	0.0455	8.34	*		0.0208	4.63
40	0.0195	5.92	0.0287	6.82	0.0408	10.17			0.0170	5.58
50	0.0158	6.75	0.0252	7.89	0.0360	11.95			0.0148	6.34
62	0.0142	7.50	0.0230	8.90		13.70			0.0130	7.13
Product N %	powder 2.34		powder 5.8		sintered very slightly 3.72		sintered slightly. >15		powder	

* N_2-pressure was changed after 20 minutes and the change of velocity with pressure was measured. The result was already reported in this bulletin, **7** (1932), 143–154.

** The carbide and the velocity unit are different from the other four; its purity is 68.2%.

It is evident from the table and figures, that addition of an active carbon not only accelerates the reaction, but also almost puts out the maximum point of velocity. In experiment No. 521 the maximum velocity did not appear after two minutes before which the velocity was not measured, while without carbon the maximum velocity appears after more than 3 minutes at this temperature. The accelerating action of carbon, especially at the earlier stage of the azotation may be recognized to be conspicuous. The action of the cyanamide at this lower temperature can also be attributed to the carbon contained in the cyanamide. It should be weak, because its quantity ($13.3 \times 0.2 = 2.66\%$) is small with respect to the carbide, and as the carbon in the cyanamide is in the form of graphite with

some amorphous carbon, and as it had been subjected to higher temperatures, the activity will be but weak. Calcium fluoride had no effect at 870°C., while calcium chloride accelerated the reaction extraordinally, which will be partly due to the action of decomposing the carbide, and setting carbon free. As to this problem, the discussion will be given later in this bulletin.

The most of these experiments were carried out in the research laboratory of the Denki-Kagaku-Kogyo Co. Ltd. Tokyo, before Sept. 10th (1930), and reported to the meeting of engineers and directors of the Co. on that day.

Summary.

The effects of some catalytic substances to the velocity of azotation of both powdered and "granular" carbide were experimentally determined.

1. There is an optimum quantity of calcium fluoride to be added to the carbide to get the highest velocity of azotation, the quantity of which is a function of both carbide and reaction temperature.
2. The added substances not only have some influence upon the velocity, but also change the characteristics of the velocity curves of azotation.
3. Carbon and carbon containing substances or those which sets carbon free from carbide show strong catalytic action to the azotation of calcium carbide. The opinion that the nascent carbon must be acting as a catalyser is supported.

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THE RELATION BETWEEN KOLBE'S REACTION AND HYDROGEN ION CONCENTRATION. VII. THE MECHANISM OF KOLBE'S REACTION.

By **Hamilton Ryoichi MATSUDA.**

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The present author's observation on the gas evolved from the solutions of potassium acetate under electrolysis, and the studies on chemical behaviours of the solutions during the electrolysis—especially their oxidizing and reducing actions—led him to the conclusion that ethane in these cases had its origin in acetyl peroxide, as already had been reported in the previous communication.[1]

(1) This Bulletin, **7** (1932), 18.

In order to examine the validity of the Peroxide Theory, electrolyses of potassium propionate solutions were carried out under nearly the same principle as in the case of the acetate solutions.

Although there is a report from another source that a highly concentrated solution of sodium propionate acidified with propionic acid produces butane in a larger quantity than ethylene[1] such is to be regarded only as an exceptional case, since ethylene, from a general point of view, may be taken as the principal product of the Kolbe's Reaction of a propionate solution. Because a concentrated solution of potassium propionate produces ethylene in an overwhelming quantity, accompanied by far less amounts of butane and ethyl propionate; and moreover, butane decreases as the concentration of the solution is lowered.[2]

As a proper sequence the present paper chiefly deals with the relation between the ethylene formation and oxidizing action of the electrolysed solution.

As is mentioned below, propionyl peroxide which can be taken as the original product of the Kolbe's Reaction of potassium propionate just as the acetyl peroxide in the case of potassium acetate, is a substance of a greater stability than the latter,[3] hence it follows that propionyl peroxide must be more resistible to the anodic actions than acetyl peroxide. It may be therefore presumed that there is formed, in this case, propionyl peroxide or certain peroxidic substances formed from it by decomposition, in quantities greater than equivalent to the corresponding peroxidic substances produced in the case of potassium acetate, thus giving a stronger oxidizing power to the propionate solution.

As are described below, the experimental facts observed by the author are all in the fullest agreement with this assumption, and exactly as in the case of the acetate, the formation of hydrogen peroxide is explained by assuming that it is produced by the hydrolyses of propionyl peroxide as shown in the following equations:

$$(C_2H_5COO)_2 + H_2O = C_2H_5COOH + C_2H_5COOOH \quad \ldots\ldots\ldots \quad (1),$$

$$C_2H_5COOOH + H_2O = C_2H_5COOH + H_2O_2 \quad \ldots\ldots\ldots\ldots\ldots \quad (2).$$

(1) Zimmermann, Dissertation, Gieszen, 1899.
(2) Petersen, *Z. physik. Chem.*, **33** (1900), 106.
(3) Acetyl peroxide: Nef, *Ann.*, **298** (1897), 289; propionyl peroxide, Clover, Richmond, *Am. Chem. J.*, **29**, 191.

Experimental.

The apparatus used for electrolysis were the same as those mentioned in the preceding papers,[1] 100 c.c. of the electrolyte having been employed each time.

Test for hydrogen peroxide: the presence of this substance was attested by means of a titanium sulphate solution.

Potassium permanganate test: 20 c.c. of the sample solution were acidified with an excess of sulphuric acid, and titrated with n/100 potassium permanganate solution.

Potassium iodide and starch test: 20 c.c. of the sample solution were added to a potassium iodide solution, and iodine that had been set free was titrated with n/100 thiosulphate solution, using a starch solution as the indicator. When reaction was considered to have ceased, a little more potassium iodide was added to ascertain that there was no recovery of the starch-iodine colour.

Table 1.

Electrolyses of dilute solutions of potassium propionate.

Electrolyte % KPr	pH		Duration of Electrolysis	Exam. of the solution			C_2H_4
	orig.	after		H_2O_2	$\frac{n}{100}KMnO_4$	KI+Starch	
0.1	6.0	6.0	12 min.	abs.	4 drops*	no reaction	0
0.3	6.1	6.1	7	,,	7	,,	,,
0.5	,,	,,	12	,,	15	,,	,,
0.7	6.2	6.3	20	,,	25	,,	,,
1.0	,,	7.9	30	pres.	70	$\frac{n}{100}Na_2S_2O_3$ 29 drops	6.5%

* 25 drops = 1 c.c.

Current density was 3.6 A/dm.^{2} at the anode in the case of 0.1% solution and 10 A/dm.^{2} in other cases. Temperature ranged 9–12°C., except in the case of 0.3% solution, which was electrolysed at 17–18°C. The gas samples were collected as follows: 35 c.c. from 0.1% solution and 60 c.c. from 0.3% solution, each during the whole course of electrolysis; but from three other solutions 60 c.c. were collected in the first six minutes.

The first four solutions were very similar to one another not only in changing their pH values but very slightly during the electrolysis but in

(1) loc. cit.

producing neither oxidizing substances nor ethylene; only difference being in their respective reducing power against potassium permanganate.

0.1 Per cent. solution was electrolysed by a current of much smaller density than that used in other solutions, that is, 3.6 A/dm^2. As was observed in the case of acetate[1] a current of greater density makes Kolbe's Reaction more difficult to occur in a very dilute solution. It was presumed by analogy that 0.1% solution of potassium propionate would never produce ethylene, if a current of greater density, such as 10 A/dm^2., were applied.

1.0 Per cent. solution differed from others in a remarkable manner in changing its pH value in a far broader range, and in producing some oxidizing substance, perhaps other than hydrogen peroxide, as well as ethylene.

It was thus found that the formation of ethylene by electrolysis of potassium propionate is always accompanied by that of some oxidizing substances, in exact analogy to the facts observed in the case of acetate-electrolysis. It was also discovered that the least necessary concentration of potassium propionate solution capable of undergoing Kolbe's Reaction lies somewhere between 0.7 and 1.0%, when worked under above mentioned conditions.

Table 2.

Electrolyses of dilute potassium propionate solutions, which contained 1 gr. ammonium carbonate per 100 c.c.

$D_A = 15$ A/dm^2., Temp. $= 8-10°$C.

Electrolyte % KPr	pH		Duration of Electrolysis	Exam. of the solution			C_2H_4
	orig.	after		H_2O_2	$\frac{n}{100}$ $KMnO_4$	KI+Starch	
0.1	8.5	8.8	5 min.	abs.	4 drops	$\frac{n}{100}$ $Na_2S_2O_3$ 3 drops	0.4%
0.3	,,	8.7	10	pres.	18	6	,,
0.5	,,	,,	15	,,	36	20	0.6
1.0	,,	,,	30	,,	10.7 c.c.	42	1.2

For analysis, 60 c.c. of the evolved gas were collected, and it took 5 minutes in the case of 0.1% solution, and $3\frac{1}{2}$–4 minutes after the start of electrolysis in every one of the other cases.

The ethylene production even from such very dilute solutions as shown above was possibly due to the addition of ammonium carbonate which caused

(1) loc. cit.

sufficient lowering of the anodic potential, raising the pH value of the solution, even under a comparatively higher current density such as $D_A = 15$ A/dm^2.

0.1 Per cent. solution formed hydrogen peroxide no more, this probably on account of its extreme smallness of concentration. While even the first solution in the above table produced ethylene, 1.0% solution produced it in a much less amount when compared with that evolved from the solution of the same concentration to which no ammonium carbonate was added (compare Tables 1 and 2). This is because the lowering of the anodic potential caused by the presence of ammonium carbonate reached such an extent that the solution became unsuitable for ethylene formation. In this case again, the ethylene formation was found always accompanied by the oxidizing action of the electrolysed solution.

The results of the electrolysis of a solution containing 5.0 gr. potassium propionate and 2.0 gr. propionic acid per 100 c.c. were as follows :

Table 3.

Electrolyte, (5.0 gr. potassium propionate+2.0 gr. propionic acid per 100 c.c.) solution,

$D_A = 15$ A/dm^2., Temp. = 8—10°C., Original pH = 5.0.

Duration of Electrolysis	Exam. of the solution				C_2H_4
	pH	H_2O_2	$KMnO_4$	KI+Starch	
15 min.	5.1	trace	n/100 2.8 c.c.	n/100 $Na_2S_2O_3$ 4 drops	26.6%
30	5.3	,,	3.8	11	26.2
45	5.9	pres.	6.0	26	,,
1 hours	7.9	,,	10.0	5.0 c.c.	27.5
2	8.5	,,	51.5	6.5	14.4
3	9.2	,,	67.5	11.0	6·2
4	9.3	,,	,,	17·0	3·4
5	,,	,,	70.0	25.5	1.7
6	9.2	,,	85.0	27.6	0.6
7	,,	,,	50.0	21.5	0.2
9	9.1	,.	32.5	14.5	

The curves in Fig. 1 represent the pH, the thiosulphate and the ethylene values given in Table 3. The values on the ethylene curve corresponding to the durations 0, 1 and 1/6, 1$^1/_2$, 2$^1/_2$ and 3$^1/_2$ hours are not given in the table.

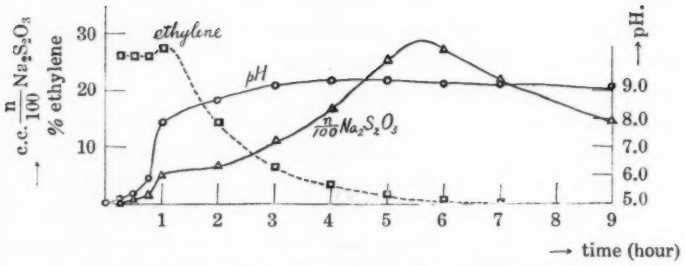

Fig. 1. Electrolyte, (5 gr. KPr + 2 gr. HPr) per 100 c.c.
D_A = 15 A/dm²., Temp. = 8–10°C.

The ethylene formation was almost constant for the first one hour, when the pH value quickly increased from 5.0 to nearly 8.0. It can be gathered from these facts that during the first hour the concentration of the propionate was always kept constant at the original value at the cost of that of the free acid. After that, the ethylene formation began to decrease, reaching almost nought in six hours, and the pH value, after rising gradually, remained almost constant at 9.3 during the last six hours of the experiment.

The thiosulphate consumption was slight for the first half an hour, the pH value of the solution remaining lower than 5.5; then it promptly and perceptively increased with the rise of the pH value; and at the same time the formation of ethylene was most abundant during this period. After this it increased gradually till at last it reached the maximum value before the ethylene formation finished.

In the case of potassium acetate the relation was entirely different. The thiosulphate consumption was always found greatly depressed by the intense ethane formation, and its maximum value was reached after the ethane formation had ceased.

In this case the presence of hydrogen peroxide was traced after 15 minutes' electrolysis, when the pH value was as low as 5.1. Its actual presence, however, became quite distinct 30 minutes later, when the pH value was 5.9. This also was entirely different in the case of above mentioned acetate solution, in which hydrogen peroxide was not detected even after 45 minutes' electrolysis, when the pH value was found to be 5.9.

The potassium permanganate consumption quickly increased throughout the second and third hours of the electrolysis. This fact indicates the gradual increase of the formation of reducing substances, chiefly caused by the rise of the pH value from 8.0 to 9.2.

The content of butane in the gas samples ranged from 0.2 to 0.6 volume %; the presence of ester in the electrolysed solution could distinctly be detected by its sweet smell. But these two substances can not be considered to play an important rôle in this electrolysis.

If the formation of ethylene is assumed to be due to the decomposition of propionic peracid according to the following equation:

$$C_2H_5COOOH = C_2H_4 + H_2O + CO_2 \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (3),$$

the decomposition reactions must be regarded to proceed in two ways, one, according to the equation (3), and the other, according to the equation (2), and these two reactions to take place side by side, to a certain extent, at the pH value ranging 8.0–9.3, and the former decomposition steadily to decline with the progress of electrolysis in contrast to the predominance of the latter.

The results of the electrolysis of a solution containing 5.0 gr. potassium propionate and 5.0 gr. ammonium carbonate per 100 c.c. are given in the following table and figure:

Table 4.

Electrolyte, (5.0 gr. potassium propionate+5.0 gr. ammonium carbonate per 100 c.c.) solution,

$D_A = 15$ A/dm², Temp. = 6—7°C., Original pH = 8.7.

Duration of Electrolysis	Exam. of the solution				C_2H_4	O_2
	pH	H_2O_2	$\frac{n}{100}$ $KMnO_4$	KI+Starch		
0 hour					14.8%	8.6%
1					14.2	
2	9.0	pres.	35.0 c.c.	$\frac{n}{100}$ $Na_2S_2O_3$ 2.7 c.c.	10.2	6.2
3					4.6	
4	8.6	pres.	41.0	7.5	3.2	8.0
6	8.5	,,	45.0	8.5	0.8	
8	8.0	,,	17.0	7.1	0.4	13.8

As no small amounts of oxygen were observed to be evolved, the internal oxidation in this solution must be taken as rather insignificant (compare with the corresponding case of the acetate, Table 7 in the previous paper, loc. cit.). The comparatively smaller values of potassium permanganate consumption conforms to this conjecture.

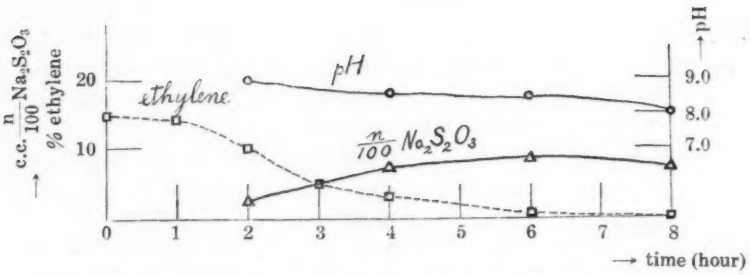

Fig. 2. Electrolyte, (5 gr. KPr+5 gr. amm. carbonate) per 100 c.c. $D_A = 15$ A/dm²., Temp. = 7°C.

The higher value of pH, and, consequently, a lower anodic potential, caused by the addition of ammonium carbonate acted unfavourably to the discharge of propionyl ion, $C_2H_5COO^-$, as indicated by the above fact, as well as by the fact that the maximum values showing the ethylene formation and thiosulphate consumption were both remarkably lower than those given in Table 3.

Hydrogen peroxide may be regarded in the present case to have been formed soon after the start of electrolysis for the reason of the higher value of pH. The coincidence between the declination of the ethylene formation and the ascendency of the thiosulphate consumption was very clearly observed : a fact which, the author is confident, amply justifies this Peroxide Theory.

In closing this seventh paper on these researches, let the author express once more his most profound thankfulness for the constant encouragement and ever helpful suggestions, which he has received throughout his somewhat prolonged studies from his old master, Professor Dr. M. Matsui of Kyoto Imperial University.

Summary.

(1) 0.1–0.7 Per cent. solution of potassium propionate gave neither ethylene nor signs that the solution had undergone any oxidation, when electrolysed by passing a current of $D_A = 10$ A/dm². at 9–12°C.

(2) When 1.0% potassium propionate solution was electrolysed under the same conditions, ethylene was produced, and at the same time oxidizing action of the solution became observable. Hydrogen peroxide was also found present.

(3) The presence of ammonium carbonate proved so effective as to produce ethylene even from the most dilute solution. Ethylene formation was always accompanied by oxidizing action of solutions in all cases alike.

(4) Electrolyses of a solution containing 5.0 gr. potassium propionate and 2.0 gr. propionic acid and the one containing 5.0 gr. potassium propionate and as much ammonium carbonate, each in 100 c.c., were investigated.

(5) The assumption of propionyl peroxide at the intermediate product provides a very satisfactory explanation of Kolbe's Reaction and also of other reaction related to it in the electrolysis of a propionate; the production of ethylene, hydrogen peroxide and similar oxidizing substances may all be explained to take place according to the following scheme:

$(C_2H_5COO)_2 + H_2O = C_2H_5COOH + C_2H_5COOOH$,

$C_2H_5COOOH = CO_2 + H_2O + C_2H_4$ (Ethylene formation),

$C_2H_5COOOH + H_2O = C_2H_5COOH + H_2O_2$ (Hydrogen peroxide formation).

(6) The difference observed between electrolyses of potassium propionate and potassium acetate will easily be understood, if we take notice of the higher stability of propionyl peroxide in comparison with acetyl peroxide.

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X-RAY STUDY ON THE ELECTROLYTIC Fe-Ni ALLOYS.

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Synopsis.

Iron and nickel were co-deposited in various proportions electrolytically from their mixed sulphate solutions, and X-ray diffraction patterns were photographed by the Debye-Scherrer and Seemann-Bohlin methods, and the lattice constants were measured by choosing lines of copper as a standard which was mixed with the alloys in the form of powder. The results obtained were as follows. (1) Iron and nickel in the deposit appears as solid solution. The homogeneity of the solid solution thus formed seems not so good as that of the alloy solidified from the melt. (2) The co-existence of α and γ solid solutions is also observed in the deposits the concentration of which ranged from 14% Ni to 58% Ni. In the alloys solidified from the melt this ranges from 25% Ni to 33% Ni. (3) Lattice constant of α or γ solid solution increases slightly at first, reaches maximum and then decreases as the constant of Ni or Fe increases respectively. From these results it has been concluded that when the total or local concentration of the one metal in the deposit is small, two cases may arrise either the metal is forced to deposit among the crystal of the other metal without forming its proper crystal lattice forming

pseudo solid solution as a result or the unit mass of the deposited crystal of that metal is small and consequently it easily diffuses into the other after the deposition. This is the reason why the lattice constant-concentration curve runs upward. But when the concentration is fairly large, the unit mass of that crystal also becomes larger and its diffusion into the other takes place not so easily as before leaving some of that crystal undiffused. This tendency becomes greater as the concentration of that metal increases. The existence of the maximum point on the curve above mentioned and the coexistence of α and γ solid solutions in a wider range of the composition of the deposited alloy are explained sufficiently by the process of deposition above supposed.

Introduction.

There is a few study on the crystal structure of the alloy[1] electrolytically co-deposited from the aqueous solution of the salts of two kinds of metal. Nakamura[2] observed by the X-ray study that the crystal of the electrolytic brass containing 17.52% of Zn co-deposited from the cyanide solution well coincides with the alloy of the same composition obtained from the melt in its form and in its lattice constant. G. Fuseya and K. Sasaki[3] also concluded by the X-ray study that the electrolytic Fe-Cr alloy containing 30% of Cr forms solid solution. As to the mechanism of these phenomena the following cases may be considered.

(1) The discharge of the two kinds of metal ion occurs at the position of each inherent crystal lattice, and not at the position of the crystal lattice of their solid solution. But as the state of mixing of the two metals in the deposit is very intimate, two metals easily diffuse with each other and form solid solution.[4]

(2) The discharge of the two kinds of metal ion occurs at the position of the crystal lattice of their solid solution, and not at the position of each inherent crystal latice when the condition of electrolysis is suitable.

(3) The two kinds of metal ion are forced to discharge at random without being allowed to choose the mode of discharge (1) or (2), and consequently the pseudo solid solution are formed the predominated metal being the solvent. In this case diffusion naturally occurs after the deposition.

By the case of brass or Fe-Cr alloy mentioned above, it is not convenient to decide which is the chief mechanism of deposition among the above three processes, because though Cu and Zn have different crystal forms they diffuse very easily with each other,[5] and though Fe and Cr do

(1) Electrolytic alloy means a mixture of two or more metals co-deposited by electrolysis.
(2) M. Nakamura, *Bul.Inst. Phys. Chem. Research, Japan, (Riken-Ihô)*, **4** (1925), 71.
(3) G. Fuseya and K. Sasaki, *J. Soc. Chem. Ind., Japan, (Kôgyô-Kagaku-kaishi)*, **33** (1930), 1337.
(4), (5) Tammann, Lehrbuch der Metallographie, 3 Auflage (1923), 233.

not diffuse so easily as the case of Cu and Zn, they have the same crystal form and the difference between the lattice constants is very small being 0.017 Å. So we have chosen the alloys of Fe and Ni to study the mechanism of deposition, and we have prepared a series of the alloy whose composition varies from 0~100% of Ni and studied their structure by the X-ray analysis. In the alloy of this system obtained from the melt up to 25% of Ni, the alloy consists of α solid solution only (body centred cubic lattice) and from 33% of Ni to 100% of Ni only of γ solid solution (face centred cubic lattice) and between 25% and 33% of Ni it consists of α and γ solid solutions (both body centred and face centred).[1]

Experimental.

Preparation of Electrolytic Fe-Ni Alloys. Co-deposition of iron and nickel by electrolysis was studied by S. Glasstone and T. E. Symes.[2] Using the chemical analysis, the composition of the alloys, prepared by the electrolysis from the mixed sulphate solution of various concentration, were determined. But whether this so called alloy was the true alloy having a definite crystal structure or not was not studied. L. E. Stout and J. Carol[3] studied the co-deposition of iron and nickel from their mixed cyanide solution, but they also did not touch the problem of the crystal structure of the deposit. For the present study, the sulphate solution was taken as the electrolyte, the total concentration of which was two normal, and to prevent the formation of ferric hydroxide in consequence of the anodic oxidation during electrolysis the electrolyte was acidified to two normal with sulphuric acid. Glasstone observed that when electrolyte is dilute in its concentration and not stirred during electrolysis for a long time, the iron contents in the deposit more or less decreases though the hydrogen ion concentration does not affect the composition of the deposit. In our experiment, electrolyte was sufficiently concentrated and stirred and in addition to these, our deposit was little in quantity compared with the total metal content in the electrolyte (total metal content 28 gr., deposit about 0.2 gr.), and so the inequality of concentration in deposit may be negligible. As the cathode thin plate of copper, 0.17 mm. in thickness and 20 cm^2. in effective area, was used and as the anode two thin plates of platinum, 3.5 cm. long and 1.5 cm. wide, were put on either side of the cathode. Electrolysis was carried out at room temperature, and C.D. was always kept at 0.02 amp/cm^2.,

(1) A. Osawa, *Kinzoku-no-Kenkyu*, **2** (1925), 809; T. Kasé, *ibid.*, **1** (1924), 1215.
(2) S. Glasstone and T. E. Symes, *Trans. Faraday Soc.*, **23** (1927), 213; **24** (1928), 370.
(3) L. E. Stout and J. Carol, *J. Am. Electrochem. Soc.*, 1930, Sept. Meeting; *Stahl .u Eisen*, **50** (1930), 1533.

electrolyte being stirred during it. Before electrolysis cathodes were well polished, washed with concentrated KOH solution, dipped in concentrated nitric acid for a few seconds, washed well with water, dipped in dilute sulphuric acid, washed with water again and then used. The volume of electrolyte was 500 c.c., the time of electrolysis 4 hours. After the electrolysis the deposit was separated from the cathode, powdered, and the one half of it was used for X-ray analysis, the other for chemical analysis and the results obtained were as follows.

Table 1.

No.	Concentration of Nickel in	
	Solution (%)	Deposit (%)
1	0	0
2	33	9
3	51	11
4	61	14
5	67	20
6	84	31
7	89	37
8	98	58
9	99	80
10	100	100

X-ray Analysis. The X-ray analysis of the above 10 specimens has been carried out by Debye-Scherrer and Seemann-Bohlin methods. The results are tabulated in Table 2, and graphically represented in Fig. 1. Some of the diffraction patterns taken by the method of Debye-Scherrer are shown in Photo. 1 as examples.

Table 2. Results of X-ray Analysis.

(a) Body-centred Lattice.

No.	% Ni	R	$h_1h_2h_3$	r	$2b$	θ (Radian)	$\sin\theta$	d	Å
1	0	27.754	211	0.263	108.629	0.977036	0.82884	1.166932	2.858_4
1′	0	27.705	,,	0.288	108.522	0.977640	0.82918	1.166456	2.857_2
2	9	27.754	,,	0.275	108.739	0.976320	0.82844	1.167496	2.859_7
3	11	27.800	,,	0.288	108.456	0.975234	0.82783	1.168354	2.861_8
4	14	27.660	,,	0.385	108.120	0.975137	0.82776	1.168454	2.862_1
5	20	27.727	,,	0.238	108.345	0.977554	0.82801	1.168101	2.861_2
6	31	27.736	,,	0.310	108.620	0.977312	0.82899	1.166720	2.857_8
7	37	27.660	,,	0.325	108.600	0.979745	0.83033	1.164838	2.853_3
8	58	27.721	,,	0.280	108.789	0.979540	0.83023	1.164972	2.853_6

(b) Face-centred Lattice.

No.	% Ni	R	$h_1h_2h_3$	r	$2b$	θ (Radian)	$\sin\theta$	d	Å
4	14	27.735	220	0.385	98.478	0.887666	0.77560	1.24703	3.527_1
5	20	27.744	,,	0.238	98.702	0.887690	0.77562	1.24701	3.527_3
6	31	27.742	,,	0.310	98.530	0.885688	0.77436	1.24903	3.532_8
7	37	27.652	,,	0.325	98.420	0.887470	0.77549	1.24721	3.527_6
8	58	27.698	,,	0.280	98.140	0.883782	0.77315	1.25099	3.538_2
9	80	27.679	,,	0.295	97.632	0.880756	0.77122	1.25411	3.545_1
10	100	27.743	,,	0.280	98.912	0.889344	0.77666	1.24534	3.522_3
10′	100	27.707	,,	0.283	98.834	0.889740	0.77691	1.24499	5.521_2

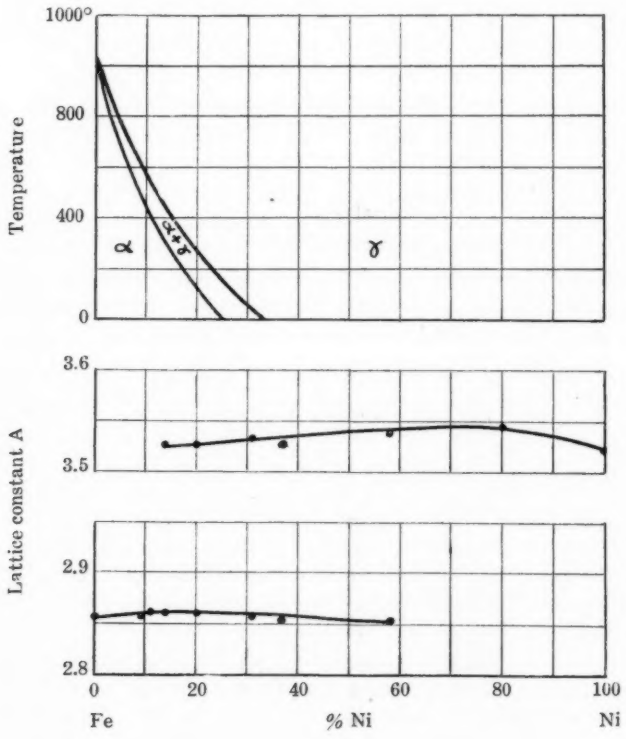

Fig. 1.

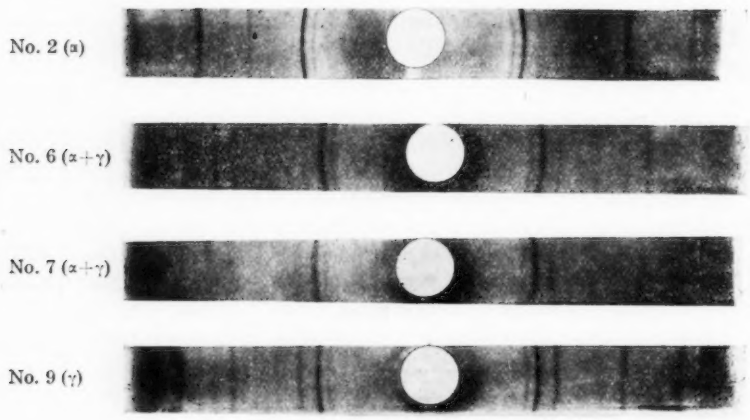

Photo. 1.

Lines in No. 2 consist of those which belong to body centred cubic lattice, lines in No. 9 consist of those which belong to face centred cubic, and in Nos. 6 and 7 we find the mixture of lines of both crystals. Lines of body centred cubic are deeper than those of face centred cubic in No. 6 and opposite in No. 7. This is due to the relative quantity of both crystals. In No. 6 and No. 7 K_α lines diffracted from the crystal plane 110 overwrap with those from the plane 111 and seem very thick and deep. To calculate the lattice constants we photographed the lines from pure Cu crystal at the same time on the same film by mixing the fine powder of Cu with the samples. As the lattice constant of Cu is known, effective radius of camera is calculated from the lines of Cu thus photographed and the lattice constants of the samples were calculated therefrom, thus avoiding the errors caused by camera, film etc. On calculating lattice constants we chose 211 K_α in the case of body centred cubic lattice and 220 K_α in the case of face centred cubic as these lines were relatively thick and not so diffused as others and their reflecting angles are large. For the former line, i.e. 211 K_α of body centred lattice, 220 K_α and 311 K_α lines of Cu are taken as a standard and for the latter line, i.e. 220 K_α of face centred lattice, 220 K_α line of Cu as a standard adopting for the lattice constant of Cu 3.603 Å.[1] The wavelength of X-ray was calculated as 1.9344 Å from two K_α lines by proportion of their intensity. The formula $-r(1+2\cos\theta)$ was used for the correction of the radius of the samples, where r meant the radius of the sample, θ

(1) Int. Crit. Tab., I, 340.

the reflecting angle, because this formula had been used in calculation of the effective radius of the camera from the lines of copper. Care was taken to measure $2b$ because the diffusion of lines caused by electrolysis was great. The lattice constants of the samples are shown in the above table in which R shows the effective radius calculated from the line of copper, the wave-length of X-ray was enacted as 1.9344 Å. In this table samples No. 1′ and No. 10′ were heated in vacuum at 600°C for 30 minutes, and others not heated.

Fig. 1 shows these results graphically. The lower part of it shows the lattice constant-concentration curve, and the upper part the equilibrium diagram of the alloy cooled from the melt.[1]

Interpretation of the Results.

1. Lattice Constants of the Electrolytic Metals and Alloys. The values of lattice constant for iron and nickel found in literature (Table 3) coincide well with ours.

Table 3.

Metal	Fe	Ni
A	2.855 ~ 2.859[2]	3.540[4]
		3.514[5]
	2.855 ~ 2.856[3]	3.514[6]

As iron and nickel electrolyzed contain much hydrogen their lattices expand about 0.001 Å as shown in the previous table. For the iron our result agrees well with other, while for the nickel our value is intermediate one among theirs. As for the lattice constants of the alloys made from the melt, we can find several studies by X-ray analysis[7] but their results don't

(1) A. Ôsawa, T. Kasé, see before.
(2) W. H. Day, *Phys. Rev.*, **25** (1925), 755. Fe_2O_3 was reduced with hydrogen.
(3) A. O. Jung, *Z. Krist.*, **65** (1927), 311. Iron was used which was prepared at Bureau of Standard, the purity of which was 99.937%.
(4) A. W. Hull, *Phys. Rev.*, **17** (1921), 579. Electrolytic nickel was used.
(5) The same with (2).
(6) L. W. McKeehan, *Phys. Rev.*, **21** (1923), 402. Mond nickel the purity of which was 99.7% was used.
(7) M. R. Andrews, *Phys. Rev.*, **17** (1921), 261; **18** (1921), 245; A. Ôsawa, *Kinzoku-no-Kenkyu*, **2** (1925), 809; A. O. Jung, see before; L. W. McKeehan, see before.

coincide with. However all of these studies coincide well with the point that their lattice constants increase in α or γ solid solution as nickel or iron content increases respectively. Contrary to this in our results lattice constants increase at first as the solute increases in its concentration, reach maximum values, and then decrease in both α and γ solid solutions. This is a remarkable difference between their cases and ours. In our preliminary experiment the same phenomena was observed with the two samples containing 42% Ni and containing 58% Ni respectively, which is shown in Fig. 2 (C, D). In this figure the intensity curves are taken with

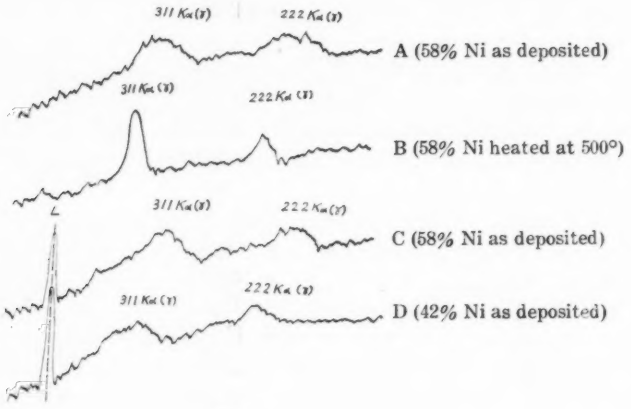

Fig. 2.

the spectral lines corresponding to the two kinds of samples above mentioned, taken on the same film. L means a line marked on the film for taking the intensity curve.

2. Diffusion of Spectral Lines of Electrolytic Alloys. It is observed that though lattice of electrolytic iron and nickel expand owing to the hydrogen, their spectral lines are not diffused so much. But in the case of Fe-Ni alloys deposited they are diffused remarkably, which seems to be due to the smallness, internal stress, and inequality of the composition etc.[1] Fig. 2 (A, B) represents the intensity curves of such lines as examples photographed by Seemann-Bohlin method. In the figure A corresponds to the sample No. 8 as electrolyzed while B corresponds to the same sample heated at 500°C. for 5 hours. As seen in the figure spectral line of B is

(1) R. Brill, *Z. Metalk.*, **75** (1930), 217.

remarkably sharper than that of A. The diffusion of the spectral lines of electrolytic alloys is also seen in Fig. 2 (C, D.).

3. Coexistence of α and γ Phases in a Wide Range. As seen in Fig. 1 the range in which α and γ solid solutions of usual alloy coexist lies between 25 and 33% of Ni, but in the electrolytic alloy this ranges from 14% to 58% of Ni. This is a second difference between the two kinds of alloys one of them deposited electrolytically and others solidified from the melt throwing a certain clue to the interpretation of the mechanism of deposition of the two metal ions.

4. Mechamism of Deposition of the Alloy. From the results of experiment explained above it may be concluded that the mechanism (2) that is, the deposition of two kinds of ions takes place at the position corresponding to their solid solution can not be supported in the case of iron and nickel deposited from sulphate solution. The results of our experiment can satisfactorily be explained by assuming that principally the mechanism (1) governs the deposition and in some cases may the mechanism (3) will also play some part, i.e. ions possibly be compelled to discharge without chance to choose the definite position. By these mechanism the results of experiment are satisfactorily explained as follows, taking the α solid solution for example. Though Fe and Ni crystallize individually, when the concentration of nickel in the deposit is small, the number of nickel atoms contained in the single nickel crystal is small, so that the diffusion of this nickel crystal into the surrounding iron crystal after the deposition can easily take place making α solid solution.

When the concentration of nickel in the deposit increases, number of atoms of nickel in single crystal and the concentration of such crystal in the deposit also increases, so the concentration of nickel in the α solid solution formed by the diffusion of nickel atoms may increase and the lattice constant increases as a result. At the same time it becomes more and more difficult to diffuse all of the Ni crystal as the latter becomes large, and thus some of nickel atoms remain undiffused. In the next step as the concentration of nickel increases, this undiffused nickel crystals may become large. Into these crystals iron atoms will be mixed by the mechanism (3). Thus γ solid solution forms.

When the concentration of nickel increases again diffusion of nickel atom into the lattice of iron decreases on the contrary, but the crystal of nickel undiffused increases, and the concentration of nickel in the body centred cubic lattice decreases. At the same time, the concentration of iron in γ solid solution increases, and the lattice constant of it also increases.

Thus lattice constant-concentration curve has maxima and the heterogeneous region of α and γ solid solution appears to be very wide having no connection with the diagram of the alloy formed from melt. And thus that one of the causes of the enormous diffusion of spectral lines of these electrolytic alloy is based upon the inhomogeneity of concentration in the solid solution seems to be possible when such a mechanism is considered.

In conclusion present writers express their hearty thanks to Dr. S. Sekito and Mr. Z. Nishiyama who kindly photographed X-ray spectral lines.

Summary.

1. Iron and nickel were co-deposited from their acidic mixed sulphate solution, and the diffraction patterns were photographed by various samples containing from 0 to 100% of nickel.

2. α and γ solid solution were observed in each sample and neither pure iron nor nickel could be found.

3. The heterogeneous region of α and γ was enormously wide compared with the alloy formed from the melt.

4. The lattice constant-concentration curve has maxima in α and γ solid solution.

5. The spectral lines of the solid solution was remarkably diffused. From these results it has been concluded that these two metals principally discharge at the position of each individual crystal lattice and in some cases discharge having no chance to choose such positions may occur, but they don't discharge at the position of the crystal lattice of solid solution of these two metals in the case experimented.

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